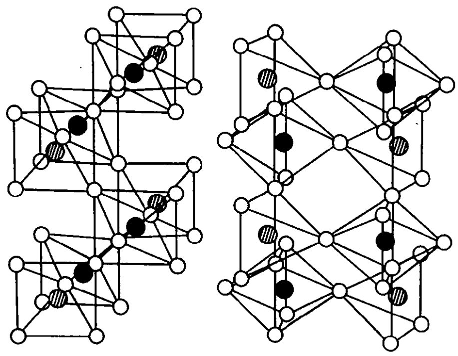

Fig. 2. Column-like units containing the double zigzag chains of Cu, O and Pt ions. Atom key: open circles O, filled circles Pt, shaded circles Cu.

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Structure of a Triclinic Rubidium Ammonium Triaqua-μ_3-oxo-hexa-μ-sulfato-triferrate(III) Tetrahydrate, $Rb_{2\cdot74}(NH_4)_{2\cdot26}Fe_3O(SO_4)_6.7H_2O$

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Abstract. $Rb_{2\cdot74}(NH_4)_{2\cdot26}Fe_3O(SO_4)_6.7H_2O$, $M_r = 1160{\cdot}9$, triclinic, $P\bar{1}$, $a = 9{\cdot}783$ (3), $b = 9{\cdot}586$ (3), $c = 18{\cdot}389$ (4) Å, $\alpha = 95{\cdot}30$ (2), $\beta = 93{\cdot}19$ (2), $\gamma = 118{\cdot}12$ (2)°, $V = 1504{\cdot}8$ (4) Å^3, $Z = 2$, $D_x = 2{\cdot}57$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 62{\cdot}3$ cm^{-1}, $F(000) = 1140$, $T = 295$ K, final $R = 0{\cdot}033$ for 4528 observed reflections. The structure contains discrete trinuclear $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units arranged in close-packed pseudotrigonal layers parallel to (001) at $z \sim 1/4$ and $z \sim 3/4$. The units are tied together by Rb and NH_4 ions which are statistically but not evenly distributed over five independent cation sites. Four Rb/NH_4 bonded water molecules complete the structure. Average bond lengths are: S—O = 1·470 (22) Å, Fe—O = 2·006 (50) Å for all types of O and 1·924 (17) Å for the oxo O atom coordinated by three Fe atoms (e.s.d.'s for individual bond lengths ≤ 0·004 Å).

Introduction. Studies in the system A_2SO_4–$Fe_2(SO_4)_3$–H_2O, where A = Na, K, Rb, Cs, NH_4 or Tl or combinations thereof, yielded many novel hydrated basic iron sulfates, many of which are now known to contain the trinuclear anion $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ as a fundamental constituent. Two subgroups of this family of salts have been investigated in some detail; the first one comprises crystals containing sodium and potassium with trigonal or hexagonal symmetry, complicated disorder phenomena and merohedral twinning (Scordari & Milella, 1983, 1984; Giacovazzo, Scordari & Menchetti, 1975), the second subgroup comprises crystals with potassium, rubidium and thallium, monoclinic symmetry and essentially ordered structures (Mereiter & Völlenkle, 1978, 1980; Mereiter, 1980). The title compound, which is pseudotrigonal triclinic in unit-cell dimensions, is of interest as a possible link between the two subgroups.

Experimental. Solutions of 2 g Rb_2SO_4, 1·5 g $(NH_4)_2SO_4$ and 4·5 g $Fe_2(SO_4)_3$ in 40 g H_2O were slowly evaporated at 340–350 K and yielded large

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yellow-brown hexagonal prisms as an intermediate product, which readily dehydrated in air and resembled Maus's salt (Giacovazzo *et al.*, 1975). Continuing with the experiment, the prisms were gradually replaced by small red-brown crystals of the title compound. They are usually richly facetted, lath-like to lens-like in shape, and stable in air. Chemical composition from qualitative tests and structure determination. Preliminary cell and space-group information from precession photographs which indicated that twinning and/or intergrowth was frequent. Further work on a Philips PW1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a single crystal ground to a sphere of 0·24 mm diameter. Accurate cell dimensions from 72 reflections, $10 < \theta < 28°$.* Data collection by θ–2θ scans, scan width 1°, θ range 2 to 27°, index range h −12 to 12, k −12 to 12 and l 0 to 23, gave 6585 independent reflections which were corrected for Lp and absorption (μR = 0·8). Three standard reflections showed insignificant fluctuations.

The structure was solved with *MULTAN*74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974), H atoms for five out of seven H_2O molecules were located by a difference map. Large block-matrix least-squares refinement on F with *SHELX*76 (Sheldrick, 1976), anisotropic temperature factors for all non-H atoms, isotropic H atoms refined as parts of rigid H_2O molecules, mixed occupation factors for alkali ion sites with total occupation factors restricted to 1, scattering functions and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Final $R = 0·033$, $wR = 0·034$, $w = [\sigma^2(F_o) + 0·00015F_o^2]^{-1}$ and $S = 1·28$ on 4528 reflections with $F_o \geq 6\sigma(F_o)$ and 436 varied parameters, $(\Delta/\sigma)_{\max} = 0·03$. $\Delta\rho$ in final difference map between −0·7 and 0·9 e Å^{-3}.

Table 1. *Atomic coordinates and isotropic thermal parameters*

$B_{eq} = 8/3\pi^2(U_{11} + U_{22} + U_{33})$, where U_{ii} are orthogonalized values.

	x	y	z	B_{eq}(Å$^2 \times 8\pi^2$)
A(1)	0·35916 (8)	0·72992 (8)	0·75793 (4)	2·43 (2)
A(2)	0·37172 (11)	0·70666 (11)	0·52236 (5)	2·62 (2)
A(3)	0·66819 (11)	0·89306 (11)	0·02417 (5)	2·69 (2)
A(4)	0·00416 (13)	0·24429 (14)	0·55361 (6)	3·43 (3)
A(5)	0·21773 (20)	0·52247 (20)	0·99352 (9)	3·15 (4)
Fe(1)	0·11033 (7)	0·63387 (7)	0·23449 (3)	1·11 (1)
Fe(2)	0·49355 (7)	0·76187 (7)	0·24105 (3)	1·06 (1)
Fe(3)	0·24965 (7)	0·38095 (7)	0·25322 (3)	0·97 (1)
S(1)	0·31758 (13)	0·87852 (13)	0·12749 (6)	1·32 (2)
S(2)	0·36355 (12)	0·93433 (12)	0·35230 (6)	1·22 (2)
S(3)	0·50115 (12)	0·48737 (13)	0·13360 (6)	1·31 (2)
S(4)	0·56483 (12)	0·57588 (13)	0·36289 (6)	1·29 (2)
S(5)	−0·04475 (12)	0·28788 (12)	0·13252 (6)	1·21 (2)
S(6)	0·01052 (13)	0·40212 (13)	0·36248 (6)	1·42 (2)
O(1)	0·1766 (4)	0·7311 (4)	0·1397 (2)	1·86 (7)
O(2)	0·4482 (4)	0·9056 (4)	0·1834 (2)	1·66 (7)
O(3)	0·2918 (4)	1·0158 (4)	0·1374 (2)	2·37 (8)
O(4)	0·3575 (4)	0·8553 (4)	0·0543 (2)	2·15 (8)
O(5)	0·2205 (4)	0·8433 (4)	0·2986 (2)	1·61 (7)
O(6)	0·4803 (4)	0·8826 (4)	0·3337 (2)	1·83 (7)
O(7)	0·4256 (4)	1·1028 (4)	0·3449 (2)	2·02 (7)
O(8)	0·3272 (4)	0·9040 (4)	0·4261 (2)	2·73 (8)
O(9)	0·5092 (4)	0·6471 (4)	0·1454 (2)	1·71 (7)
O(10)	0·4183 (4)	0·3951 (4)	0·1929 (2)	1·51 (7)
O(11)	0·6579 (4)	0·5050 (4)	0·1406 (2)	2·14 (8)
O(12)	0·4188 (4)	0·4080 (4)	0·0619 (2)	2·48 (8)
O(13)	0·6031 (4)	0·6765 (4)	0·3016 (2)	1·39 (7)
O(14)	0·4001 (4)	0·4468 (4)	0·3454 (2)	1·82 (7)
O(15)	0·6687 (4)	0·5079 (4)	0·3660 (2)	2·50 (8)
O(16)	0·5792 (4)	0·6730 (4)	0·4312 (2)	3·06 (9)
O(17)	0·0924 (4)	0·2760 (4)	0·1638 (2)	2·06 (7)
O(18)	−0·0414 (4)	0·4338 (4)	0·1704 (2)	2·45 (7)
O(19)	−0·1898 (4)	0·1521 (4)	0·1455 (2)	2·12 (7)
O(20)	−0·0373 (4)	0·2991 (5)	0·0549 (2)	2·91 (9)
O(21)	0·0788 (4)	0·3179 (4)	0·3178 (2)	1·84 (7)
O(22)	0·0148 (4)	0·5323 (4)	0·3230 (2)	2·72 (9)
O(23)	−0·1500 (4)	0·2897 (4)	0·3687 (2)	2·77 (9)
O(24)	0·0994 (5)	0·4692 (5)	0·4339 (2)	4·15 (10)
O(25)	0·2822 (3)	0·5912 (3)	0·2438 (2)	0·95 (6)
O(26*w*)	0·0675 (4)	0·6944 (4)	0·2258 (2)	2·34 (8)
O(27*w*)	0·7187 (4)	0·9368 (4)	0·2375 (2)	2·50 (8)
O(28*w*)	0·2205 (4)	0·1509 (4)	0·2596 (2)	1·49 (7)
O(29*w*)	0·0501 (4)	0·0669 (4)	0·6760 (2)	3·26 (9)
O(30*w*)	0·2014 (5)	0·9892 (5)	0·5744 (2)	3·50 (9)
O(31*w*)	0·1847 (6)	0·1828 (6)	0·4438 (3)	6·22 (10)
O(32*w*)	0·0585 (7)	0·1326 (8)	0·9354 (4)	11·11 (25)

Occupancy factors for *A* sites (*A* = Rb + NH_4)

	Rb	NH_4
A(1)	0·73 (1)	0·27 (1)
A(2)	0·58 (1)	0·42 (1)
A(3)	0·57 (1)	0·43 (1)
A(4)	0·53 (1)	0·47 (1)
A(5)	0·33 (1)	0·67 (1)

Discussion. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2.†

The structure contains the trinuclear unit $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ shown in Fig. 1. This unit consists of three strongly distorted FeO_6 octahedra which are linked by the central oxo atom O(25) and by six bridging SO_4 groups. The water molecules $H_2O(26w)$, $H_2O(27w)$ and $H_2O(28w)$ complete the coordination of Fe. Bond lengths and angles within the unit show the same trends as in previously studied salts; Fe—O bonds to the central oxo atom O(25) are short, to the SO_4 groups intermediate and to the terminal water molecules large; S—O bonds are significantly elongated for Fe-bonded O atoms and short for the rest; O_{oxo}—Fe—O_S angles are systematically larger than the O_w—Fe—O_S angles. The mean values of these types of bonds and angles are, for the title compound, 1·924 (19), 2·009 (21), 2·079 (24), 1·491 (5), 1·449 (5) Å, 95·2 (31) and 84·8 (28)°. Almost identical values were found for β-$K_5Fe_3O(SO_4)_6.10H_2O$ (Mereiter & Völlenkle, 1978) in which a $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit of similar conformation as in the title compound is present. This similarity concerns in particular the twist of the FeO_6 octahedra about their O_{oxo}—Fe—O_w axes (Fig.

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* Transformation to standardized cell: $a_{st} = c$, $b_{st} = a$, $c_{st} = b$.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52608 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Coordination of the alkali ions; the alkali-ion sites are statistically occupied by Rb^+ and NH_4^+ (*A*—O distances ≤ 3·3 Å are given)

$A(1) = 0\cdot73$ Rb + 0·27 NH_4	
A(1)—O(2^{i})	3·129 (4)
—O(7^{i})	2·899 (4)
—O(10^{ii})	3·072 (4)
—O(11^{ii})	3·006 (4)
—O(15^{ii})	2·975 (4)
—O(18^{iii})	3·179 (4)
—O(19^{iii})	2·983 (4)
—O(23^{iii})	2·945 (4)
Mean	3·024

$A(2) = 0\cdot58$ Rb + 0·42 NH_4	
A(2)—O(7^{i})	2·907 (4)
—O(8)	2·865 (4)
—O(15^{ii})	2·950 (4)
—O(16)	2·816 (4)
—O(23^{iii})	3·043 (4)
—O(24)	2·836 (4)
Mean	2·903

$A(3) = 0\cdot57$ Rb + 0·43 NH_4	
A(3)—O(3^{iv})	3·167 (4)
—O(4)	2·977 (4)
—O(4^{iv})	3·023 (4)
—O(9)	3·294 (4)
—O(12^{v})	2·872 (4)
—O(19^{vi})	2·908 (4)
—O(32*w*^{ii})	2·863 (7)
Mean	3·015

$A(4) = 0\cdot53$ Rb + 0·47 NH_4	
A(4)—O(8^{iii})	2·925 (4)
—O(15^{ii})	3·119 (4)
—O(22^{iii})	3·048 (4)
—O(24)	3·094 (4)
—O(29*w*)	3·078 (4)
—O(30*w*^{iii})	2·975 (5)
—O(31*w*)	2·950 (6)
Mean	3·027

$A(5) = 0\cdot33$ Rb + 0·67 NH_4	
A(5)—O(4^{vii})	2·891 (4)
—O(11^{ii})	2·855 (4)
—O(12^{vii})	2·944 (4)
—O(20^{vii})	2·794 (4)
—O(20^{iii})	3·128 (4)
Mean	2·922

(*b*) FeO_6 octahedra; angles in matrix representation, e.s.d.'s = 0·2°

Fe(1)—O(25)	1·911 (3)	O(25)	O(26*w*)	O(1)	O(5)	O(18)
—O(26*w*)	2·080 (4)	176·7				
—O(1)	2·045 (4)	91·9	87·0			
—O(5)	1·991 (4)	94·5	82·5	94·1		
—O(18)	1·994 (4)	98·6	84·5	86·7	166·9	
—O(22)	2·019 (4)	95·5	85·8	172·0	88·5	89·1
Mean	2·007					

Fe(2)—O(25)	1·947 (3)	O(25)	O(27*w*)	O(2)	O(6)	O(13)
—O(27*w*)	2·055 (4)	178·3				
—O(2)	2·003 (4)	100·0	81·3			
—O(6)	2·015 (4)	90·9	90·3	88·5		
—O(9)	2·039 (4)	90·3	88·5	89·5	177·9	
—O(13)	1·980 (4)	97·4	81·4	162·4	88·7	92·9
Mean	2·007					

Fe(3)—O(25)	1·913 (3)	O(25)	O(28*w*)	O(10)	O(14)	O(17)
—O(28*w*)	2·102 (4)	177·3				
—O(10)	1·998 (4)	95·3	82·1			
—O(14)	2·022 (4)	95·4	85·2	89·6		
—O(17)	2·009 (4)	94·7	84·7	90·0	169·8	
—O(21)	1·993 (4)	98·2	84·4	166·4	87·5	90·5
Mean	2·006					

(*c*) SO_4 tetrahedra

S(1)—O(1)	1·485 (4)	S(2)—O(5)	1·494 (4)
S(1)—O(2)	1·500 (4)	S(2)—O(6)	1·488 (4)
S(1)—O(3)	1·450 (4)	S(2)—O(7)	1·456 (4)
S(1)—O(4)	1·449 (4)	S(2)—O(8)	1·443 (4)
Mean	1·471	Mean	1·470
S(3)—O(9)	1·490 (4)	S(4)—O(13)	1·499 (4)
S(3)—O(10)	1·493 (4)	S(4)—O(14)	1·490 (4)
S(3)—O(11)	1·458 (4)	S(4)—O(15)	1·444 (4)
S(3)—O(12)	1·444 (4)	S(4)—O(16)	1·451 (4)
Mean	1·471	Mean	1·471
S(5)—O(17)	1·488 (4)	S(6)—O(21)	1·490 (4)
S(5)—O(18)	1·489 (4)	S(6)—O(22)	1·486 (4)
S(5)—O(19)	1·456 (4)	S(6)—O(23)	1·445 (4)
S(5)—O(20)	1·445 (4)	S(6)—O(24)	1·444 (4)
Mean	1·470	Mean	1·466

(*d*) Coordination of the oxo O(25)

				Fe—Fe
O(25)—Fe(1)	1·911 (3)	Fe(1)—O(25)—Fe(2)	119·9 (2)	3·341 (1)
O(25)—Fe(2)	1·947 (3)	Fe(1)—O(25)—Fe(3)	120·9 (2)	3·327 (1)
O(25)—Fe(3)	1·913 (3)	Fe(2)—O(25)—Fe(3)	119·1 (2)	3·328 (1)

Table 2 (*cont.*)

(*e*) Hydrogen bonds

Donor Acceptor	
O(26*w*)—O(11^{viii})	2·716 (5)
—O(29*w*^{iii})	2·713 (5)
O(27*w*)—O(19^{vi})	2·645 (5)
—O(29*w*^{ii})	2·708 (5)
O(28*w*)—O(3^{ix})	2·775 (5)
—O(7^{ix})	2·712 (5)
O(29*w*)—O(28*w*^{x})	2·892 (5)
—O(30*w*^{ix})	2·707 (6)
O(30*w*)—O(16^{i})	2·939 (6)
—O(23^{iii})	2·794 (6)

Symmetry code: none x, y, z; (i) $1-x, 2-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 2-y, -z$; (v) $1-x, 1-y, -z$; (vi) $1+x, 1+y, z$; (vii) $x, y, 1+z$; (viii) $x-1, y, z$; (ix) $x, y-1, z$; (x) $-x, -y, 1-z$.

1*a*) and, somewhat less, the orientations of the SO_4 groups. It is interesting to note that the $Fe(2)O_6$ octahedra, which show the most pronounced twist in both compounds, also stand out by their large Fe—O_{oxo} bonds [title compound 1·947 (3) Å, potassium compound 1·945 (4) Å]. More distorted $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units than in the title compound are known from $Rb_5Fe_3O(SO_4)_6.5H_2O$ and $K_{2\cdot64}Tl_{2\cdot36}Fe_3O(SO_4)_6.5H_2O$ (Mereiter & Völlenkle, 1980; Mereiter, 1980), more regular units with C_{3v} symmetry from salt *X* and related compounds (Scordari & Milella, 1983, 1984).

The arrangement of the two $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units which are present within one unit cell of the title compound and their interconnection by alkali ions and water molecules is displayed in Fig. 2(*a*). The alkali ions, 2·74 Rb and 2·26 NH_4 per formula unit, are statistically but not evenly distributed over five different *A* sites. Coordination numbers (CN, for distances ≤ 3·3 Å) and molar proportions Rb/NH_4 decrease somewhat from CN = 8 and Rb/NH_4 = 0·73/0·27 for site *A*(1), through intermediate values of CN = 6–7 and Rb/NH_4 ~ 0·56/0·44 to CN = 5 and Rb/NH_4 = 0·33/0·67 for site *A*(5). The selectivity of the five sites for a particular cation is considerably smaller than in $K_{2\cdot64}Tl_{2\cdot36}Fe_3O(SO_4)_6.5H_2O$, where the cation sites showed mixed occupation with molar proportions between 0·96/0·04 and 0·09/0·91 K/Tl. This finding is in correspondence with the ionic radii, which between Rb and NH_4 differ less than between K and Tl (Khan & Baur, 1972; Shannon, 1976). The coordination figures are irregular polyhedra for *A*(1), *A*(3), and *A*(4), a distorted octahedron for *A*(2), and, disregarding one O atom with *A*—O > 3 Å, a distorted tetrahedron of sulfate O atoms for *A*(5) (Fig. 2). This last site, which is most preferred by NH_4, offers favourable conditions for the formation of straight N—H···O bonds.

For five of the seven different water molecules of the structure H atoms could be located and corresponding hydrogen bonds are listed in Table 2(*e*).*

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* See deposition footnote.

The molecules $H_2O(26w)$, $H_2O(27w)$ and $H_2O(28w)$ are strongly polarized by Fe^{3+} and therefore form comparatively short O—H···O bonds. The last of these three also accepts a hydrogen bond and simultaneously shows the largest Fe—O distance. $H_2O(29w)$ is located between three FeO_6 octahedra and firmly anchored *via* four hydrogen bonds and an interaction with *A*(4) (Fig. 2*a*). The remaining three molecules are also bonded to each alkali ion, but only $H_2O(30w)$ is involved in well defined hydrogen bonds. O(31*w*) and O(32*w*) lack comparable interactions and therefore exhibit large thermal vibration parameters.

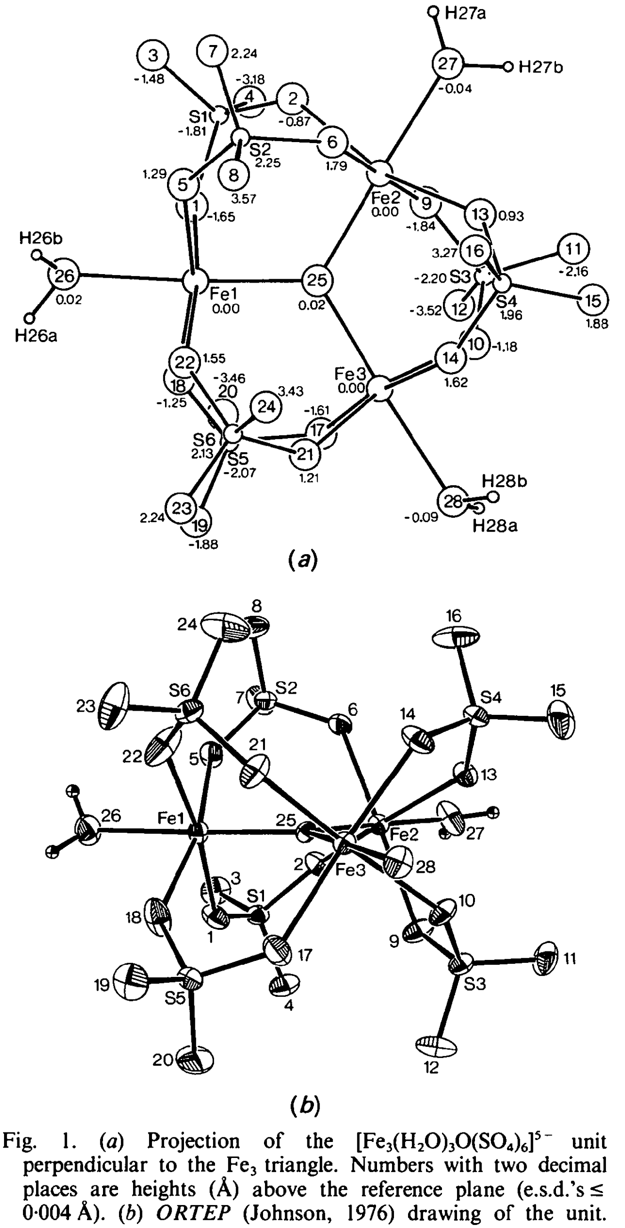

Fig. 1. (*a*) Projection of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit perpendicular to the Fe_3 triangle. Numbers with two decimal places are heights (Å) above the reference plane (e.s.d.'s ≤ 0·004 Å). (*b*) *ORTEP* (Johnson, 1976) drawing of the unit. Ellipsoids scaled to enclose 50% probability, H atoms of O(28*w*) omitted.

In the title compound the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units are arranged in two-dimensional close-packed layers which extend at $z \sim 1/4$ and $z \sim 3/4$ parallel to (001) and show trigonal pseudosymmetry (Fig. 2*b*). The alkali cations *A*(3) and *A*(5) at $z \sim 0$, *A*(1) at $z \sim 1/4$, and *A*(2) and *A*(4) at $z \sim 1/2$ tie the units together in three dimensions. The water molecules $H_2O(29w)$–$H_2O(32w)$ are concentrated in continuous channel-like spaces extending about $x, y \sim 0$ parallel

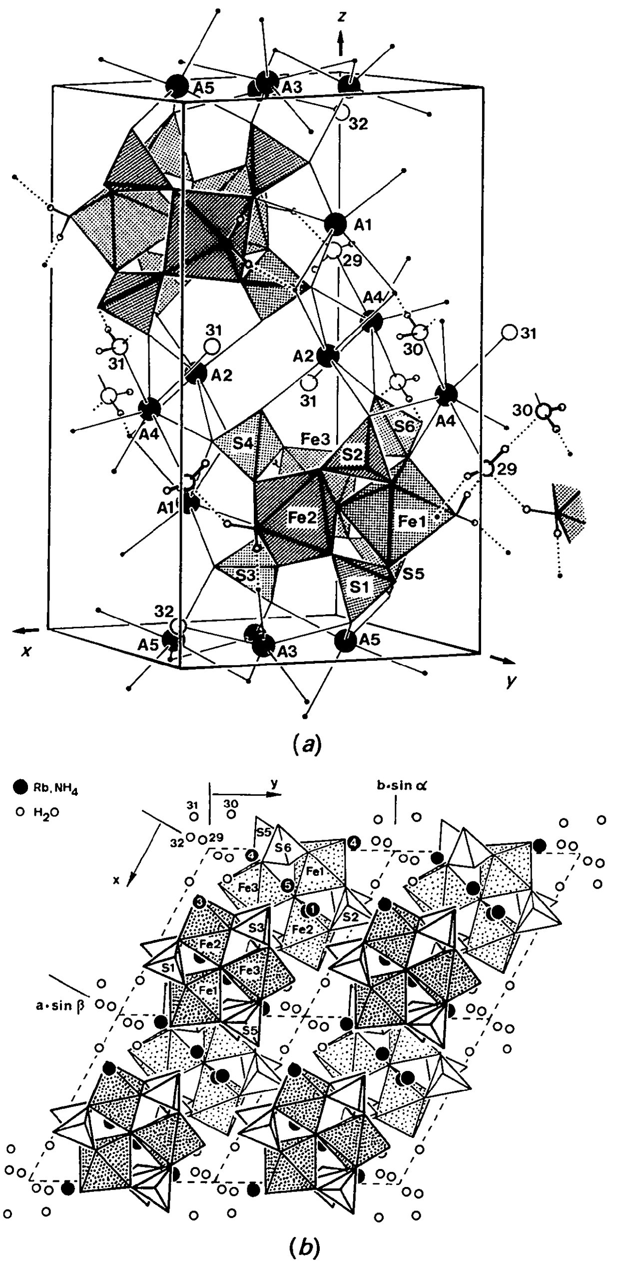

Fig. 2. (*a*) View of one unit cell approximately down **b***. (*b*) Packing diagram showing four unit cells in a projection parallel to **c**.

to *z*. The way in which the layers of $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units are stacked above each other, corresponds very well to a three-dimensional hexagonal close packing if one considers only a pair of layers at $z \sim 1/4$ and $z \sim 3/4$. This means that each unit at $z \sim 3/4$ is stacked almost perfectly above a void between three units at $z \sim 1/4$ when viewed down **c*** (deviation only ~0·2 Å). This relationship is not valid, however, between layers at $z \sim 1/4$ and $z \sim -1/4$. Compared with close-packing they are displaced relative to each other by about 2·6 Å parallel to [560]. Owing to this displacement, the pseudo-trigonal triclinic unit cell is distinctly skew in a view perpendicular to the given direction (angle between **c** and **c*** is 8·37°). Trigonal pseudosymmetry, which stems from the arrangement of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units, is further diminished by the irregular arrangement of the alkali cations at $z \sim 0$ and $z \sim 1/2$, by the water molecules $H_2O(30w)$–$H_2O(32w)$, and by the asymmetric conformation of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit. The macroscopic result of this is that crystals of the title compound do not show obvious trigonal or hexagonal aspects in habit.

The title compound differs distinctly in architecture from the monoclinic phases β-$K_5Fe_3O(SO_4)_6.10H_2O$, $Rb_5Fe_3O(SO_4)_6.5H_2O$ and $K_{2\cdot64}Tl_{2\cdot36}Fe_3O(SO_4)_6.5H_2O$, but shows close relationships to salt *X*, $(Na,K,H_3O^+)_5Fe_3O(SO_4)_6.8\cdot5H_2O$, trigonal, space group $P\overline{3}$, $a = 9\cdot643$, $c = 18\cdot018$ Å, $Z = 2$ (Scordari & Milella, 1984), and to the mineral metavoltine, $KNa_3Fe^{2+}_{0\cdot5}Fe_3O(SO_4)_6.9H_2O$, trigonal, space group *P*3 or $P\overline{3}$, $a = 9\cdot58$, $c = 18\cdot17$ Å, $Z = 2$ (Giacovazzo, Scordari, Todisco & Menchetti, 1976). In their structures $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units are centered at $x = \pm 1/3$, $y = \pm 2/3$, $z \sim \pm 1/4$, and thus adopt an almost perfect hexagonal close-packed arrangement, not violated by displacements as in the title compound. In salt *X* one potassium ($x = \pm 1/3$, $y = \pm 2/3$, $z = \pm 0\cdot78$), a sodium ($x = \pm 1/3$, $y = \pm 2/3$, $z = \pm 0\cdot52$) and a Fourier peak interpreted as an H_3O^+ ion ($x = y = 0$, $z = \pm 0\cdot86$) correspond in positions and function to *A*(1), *A*(2) and $H_2O(29w)$ in the title compound. The remaining cations (Na, K and postulated H_3O^+) and water molecules in salt *X* are located near $z \sim 0$ and $z \sim 1/2$, as in the title compound, but show a complicated disorder.

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Structure of $Ag_{0\cdot6}NbS_2$

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Abstract. Silver niobium sulfide, $Ag_{0\cdot6}NbS_2$, $M_r = 223\cdot48$, hexagonal, $P6_3/mmc$, $a = 3\cdot354\,(1)$, $c = 14\cdot431\,(1)$ Å, $V = 140\cdot59\,(6)$ Å^3, $Z = 2$, $D_x = 5\cdot279$ g cm^{-3}, $\lambda(\text{Mo } K\overline{\alpha}) = 0\cdot71073$ Å, $\mu = 93$ cm^{-1}, $F(000) = 203\cdot9$, $T = 295$ K, $R_F = 0\cdot037$ for 335 observed reflections with $I \geq 3\cdot0\sigma(I)$. This single-crystal study confirms the space-group symmetry known from powder data. The structure is based on NbS_2 sandwiches, between which Ag is statistically distributed in the tetrahedral holes.

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